

Chemistry of Sulfur-Containing Molecules on Surfaces of Molybdenum Carbide

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Introduction: Sulfur-containing molecules are common impurities in fossil fuels. In our industrial society, these impurities have a negative impact in the processing of oil-derived chemical feedstocks and degrade the quality of the air by forming sulfur oxides (SO_x) during the burning of fuels. In petroleum refineries, organosulfur molecules are removed from the oil by reaction with hydrogen to form H_2S and hydrocarbons (hydrodesulfurization or HDS processes). More stringent environmental regulations stress the need to develop a new generation of HDS catalysts that lead to the ultimate goal of clean burning fuels. Molybdenum-carbide catalysts can be useful in this respect [1,2].

Methods and Materials: Synchrotron-based high-resolution photoemission (PE) and x-ray absorption near-edge spectroscopy (XANES) were used to study the chemistry of thiophene, H_2S , CH_3SH and SO_2 on carbide-modified $\text{Mo}(110)$ and powders of Mo_2C [1,2].

Results: These studies reveal that molybdenum carbide is very reactive towards sulfur-containing molecules, being able to break S-O, S-H and S-C bonds at temperatures below 300 K. Thiophene adsorbed molecularly on MoC_x at 100 K. By 200 K, chemisorbed thiophene and its decomposition products (S and C_xH_y fragments) coexisted on the MoC_x surface. At 250 K, no C-S bonds were left [1]. There was a continuous transformation of the C_xH_y fragments into atomic C at temperatures between 300 and 800 K. Upon adsorption of sulfur dioxide on molybdenum carbide at 150 or 300 K, there is dissociation of the adsorbate into S and O, and also formation of SO_3 or SO_4 by reaction with O adatoms or disproportionation of SO_2 [2]. The adsorbed SO_3 and SO_4 species decompose upon heating to 500 K leaving a heavily sulfided and oxidized carbide. In the case of H_2S adsorption, the cleavage of the first S-H bond occurs at 80-100 K and the resulting HS intermediate transforms into S at temperatures below 250 K. Finally, for CH_3SH on MoC_x , the breaking of the C-S bonds takes place at temperatures between 250 and 400 K. From 100-350 K, CH_3S and a second S-containing species (CH_yS) coexist on the surface of the carbide. A comparison to results reported in the literature indicates that the chemical reactivity of molybdenum carbide is similar to that of metallic molybdenum and much larger than that of molybdenum sulfide (the most common compound used as a precursor for HDS catalysts). The differences in the chemical reactivities of molybdenum carbide and molybdenum sulfide correlate well with changes in the electronic properties of Mo in these systems [1,2].

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References:

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